PURDUE UNIVERSITY
Discovery Park Energy Center

Purdue Hydrogen Systems Laboratory
Part II: Hydrogen Storage

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ST084

Overview

Timeline

Start–September 2006
End–September 2010
80% complete

Budget

- $3,659,403*
  - $2,875,500 (DOE)
  - $50,000 (FFRDC)
  - $733,903 (Cost Share)
- Funding received in FY09
  $951,500

* **This is the overall budget for both hydrogen production and storage research. This presentation only covers the storage part.**

Barriers

Barriers addressed

- A. System weight and volume
- R. Regeneration processes
- S. By-product/spent material removal

Targets

		2010	2015	Ultimate
Gravimetric capacity	kgH_2/kg (wt%)	0.045 (4.5%)	0.055 (5.5%)	0.075 (7.5%)
Volumetric capacity	kgH_2/L	0.028	0.040	0.07
Overall efficiency of off-board regeneration	%	> 60	> 60	> 60

Partners

- General Motors (lab infrastructure)
- General Atomics (AB synthesis)

Project Objectives - Relevance

Ammonia Borane (AB) Recycling

- Develop an energy efficient recycling protocol for AB from ammonium borate.
- Study the conversion of ammonium borate to $B(OMe)_3$, $B(OCOR)_3$ and $B(OSO_2R)_3$ (R = CH_3, CF_3, Ph etc.).
- Study the reduction of $B(OMe)_3$, $B(OCOR)_3$ and $B(OSO_2R)_3$ to AB using Bu_3SnH or silanes.

Dehydrogenation of AB Slurry

- To analyze the engineering performance of the AB slurry based systems, including gravimetric and volumetric capacities, hydrogen release rates, and byproduct removal.
- Determine operational requirements with neat AB then apply to slurry

Investigation of Noncatalytic AB Hydrothermolysis

- Advance non-catalytic hydrothermolysis of AB in aqueous slurries and in liquid carriers.
- Investigate neat AB thermolysis.
- Develop a laboratory scale hydrogen generation unit for fuel cell system.

Approach

AB Recycling

- The spent fuel, ammonium borate will be converted to boron tris(triflate) or boron tris(trifluoroacetate), which will provide molecules with weaker B-O bond.
- Further reduction of boron tris(triflate) or boron tris(trifluoroacetate) in the presence of a trialkyl amine, followed by the displacement of the amine using ammonia will lead to efficient ammonia borane regeneration.

Dehydrogenation of AB Slurry

- Simulate the coupled heat/mass transfer and chemical reaction processes in a AB slurry reactor using in-house and commercial CFD programs.
- Two-step approach: (1) design, test, and analyze a neat AB reactor module, (2) Use lessons learned in step 1 to guide modeling and design of a slurry based reactor.
- Simulate the thermo-fluid processes in all components of the AB slurry system and the overall system behavior.

Approach (cont'd)

Investigation of Noncatalytic AB Hydrothermolysis

- Conduct and optimize non-catalytic hydrothermolysis of AB in aqueous solutions and slurries, over a wide range of AB concentrations, at different temperatures (85-135ºC) and pressures (1-15 atm) in a small size (70 ml) reactor to understand the effect on H_2 yield, ammonia generation, thermal characteristics and reaction products.
- Test and assess neat AB thermolysis near PEMFC operating temperature.
- Select and test suitable liquid carriers for AB hydrothermolysis.
- Develop, test and analyze a laboratory scale fuel cell system, based on AB dehydrogenation.

Milestones

Month/Year	Milestone or Go/No-Go Decision
Jul-10	Milestone: Develop the optimal conditions to convert the spent borate to acylborates.
Sep-10	Milestone: Reduction of acylborates using silanes in the presence of trialkyl amine.
Apr-10	Milestone: complete reactor simulation
Dec-10	Milestone: complete system engineering analysis
Sept-10	Milestone: complete tests of subscale neat AB reactor module
Dec-10	Milestone: complete design of subscale AB slurry reactor
Mar-10	Milestone: Investigate and assess neat AB thermolysis.
Jun-10	Milestone: Investigate hydrothermolysis of AB slurries using carrier liquids.
Sep-10	Milestone: Develop and test a laboratory scale fuel cell power generation system, based on AB dehydrogenation.

Previous Technical Accomplishments

AB Recycling

- Reduction of trimethyl borate using diethylsilane in the presence of TMEDA to obtain TMEDA-bisborane complex was examined.
- Regeneration of AB from TMEDA-bisborane complex via transamination was attempted.

Dehydrogenation of AB Slurry

- Achieved 92% hydrogen yield in a (1:2) AB/water slurry hydrolysis test, which provided a material based hydrogen storage capacity of 8.2 wt.%.
- Measured rheological properties of AB and SBH hydrolysis spent fuels quantitatively for the first time.
- Observed extremely fast dehydrogenation rate when measuring the AB/bmimCl slurry thermolysis process in a continuous manner.
- Determined reaction kinetics of neat thermolysis of a 0.13 g batch of AB with a starting reaction temperature of 428 K (155°C)

Investigation of Noncatalytic AB Hydrothermolysis

- Completed hydrothermolysis experiments with AB aqueous solutions over wide range of concentration, pressure and temperature conditions.
- Investigated the mechanistic basis of AB hydrothermolysis using isotopic labeling.
- Determined the optimum AB concentration where maximum H_2 can be obtained from hydrothermolysis near PEM fuel cell temperature.

Technical Accomplishments and Progress

Preparation of AB for the first feed: Past accomplishments and current breakthrough

$$2\ NaBH_4 + (NH_4)_2SO_4 \xrightarrow[\text{40 }^{o}\text{C, 2 h}]{\text{THF}} 2\ NH_3\text{-}BH_3 + Na_2SO_4 + 2\ H_2$$

96%

The dilution of the reaction medium (0.165 M) remained an obstacle for generation of AB in large scale.

$$NaBH_4 + HCO_2NH_4 \xrightarrow[\text{40 }^{o}\text{C, 2 h}]{\text{Dioxane}} NH_3BH_3 + NaHCO_2 + H_2$$

95%

- Dioxane is carcinogenic.
- The removal of dioxane and recycling is tedious.

P.V. Ramachandran & P. Gagare *Inorg. Chem.* **2007**, *46,* 7810

The synthesis of AB in liquid NH_3 was reported by Autrey and co-workers in 0.7 g scale.

$$NaBH_4 + NH_4Cl \xrightarrow[\text{-78 °C}]{NH_3} NH_3\text{-}BH_3 + NaCl + H_2$$

99%

The low temperature of the reaction could be a challenge/cost energy for scale-up.

T. Autrey et. al. *Energy Environ. Sci.*, **2008**, *1*, 156

Technical Accomplishments and Progress (cont'd)

Kilogram scale preparation of AB: Optimization of reaction condition

We have developed a novel procedure to prepare kilogram quantities of AB in THF containing 5% NH_3 at **room temperature.** (collaborator **General Atomics**)

Entry	$NaBH_4$:NH_4X	%NH_3 in THF	Ammonium salt	Yield %
1	1:2	2.5	NH_4OAc	77
2	1:1	2.5	$(NH_4)_2CO_3$	77
3	1:2	2.5	NH_4F	74
4	1:2	2.5	NH_4NO_3	50
5	1:2	2.5	NH_4HCO_2	74
6	1:2	2.5	NH_4Cl	71
7	1:1	2.5	NH_4HCO_3	71
8	1:1	2.5	$(NH_4)_2SO_4$	74
9	**1:1**	**5**	**$(NH_4)_2SO_4$**	**92**

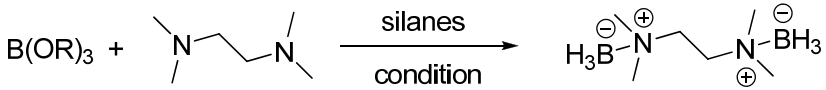
$$2\,NaBH_4 + (NH_4)_2SO_4 \xrightarrow[\text{THF, 0-10°C, 3 h, RT, 8 h}]{5\%\ NH_3} 2\,NH_3BH_3 + Na_2SO_4 + 2\,H_2$$

92%

- AB was prepared in 92% yield and ≥ 98% purity. This process was repeated several times.

Technical Accomplishments and Progress (cont'd)

Reduction of $B(OR)_3$: Optimization of reaction condition

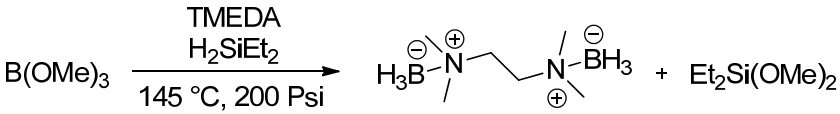


R	Silanes	Amine	H_2 Press. Psi	Temp. (°C)	Time (h)	Yield (%)
Me	$(Ph)_3SiH$	TMEDA	200	145	24	NR
Me	$(Me)_3SiH$	TMEDA	200	145	24	NR
Me	$(Ph)_2MeSiH$	TMEDA	200	145	24	NR
Me	$(Me)_2PhSiH$	TMEDA	200	145	24	NR
Me	Et_2SiH_2	TMEDA	200	145	24	78
Me	Et_2SiH_2	Et_3N	200	145	24	NR
Me	Et_2SiH_2	iPr_2EtN	200	145	24	NR

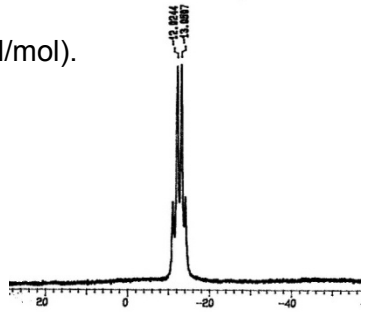
R	Silanes	Amine	H_2 Press. Psi	Temp. (°C)	Time (h)	Yield (%)
Me	Et_2SiH_2	TMEDA	200	120	24	NR
Me	**Et_2SiH_2**	**TMEDA**	**200**	**145**	**12**	**90**
Me	Et_2SiH_2	TMEDA	160	145	12	NR
$COCF_3$**	Et_2SiH_2	TMEDA	200	145	24	*
SO_2CF_3	Et_2SiH_2	TMEDA	200	145	24	*
COPh	Et_2SiH_2	TMEDA	200	145	24	*
$COCH_3$	Et_2SiH_2	TMEDA	200	145	24	*

* Charred material was obtained.

** $B(OCOCF_3)_3$ is expected to be more reactive than $B(OMe)_3$ with silane (ΔH= 7.6 Vs -7.7 Kcal/mol). Further optimization is required.



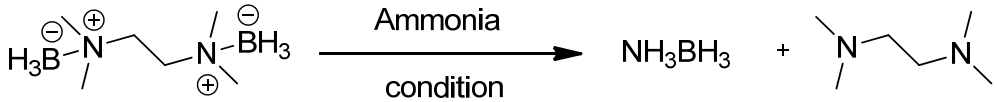
> 90% yield



Technical Accomplishments and Progress (cont'd)

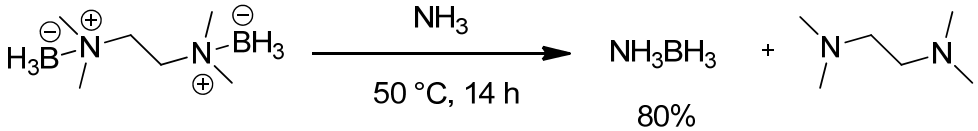
Transamination: Optimization of reaction condition

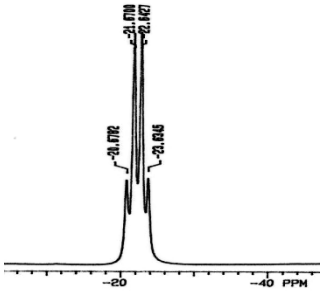
We have achieved the transamination of TMEDA-bisborane to AB in 80% yield.



Entry	Reagent/Solvent	Condition	Yield[a]	
			^{11}B NMR	Isolated %
1	Liq. NH_3/THF	35 °C, 100 Psi H_2, 24 h	100	65
2	Liq. NH_3/THF	50 °C, 200 Psi H_2, 12 h	100	82
3	**Liq. NH_3/THF**	**50 °C, 14 h**	**100**	**80**
4	Liq. NH_3/THF	50 °C, 150 Psi H_2, 12 h	100	76
5	Liq. NH_3/THF	50 °C, 200 Psi H_2, 24 h	100	85

[a] Yields after crystallization





Technical Accomplishments and Progress (cont'd)

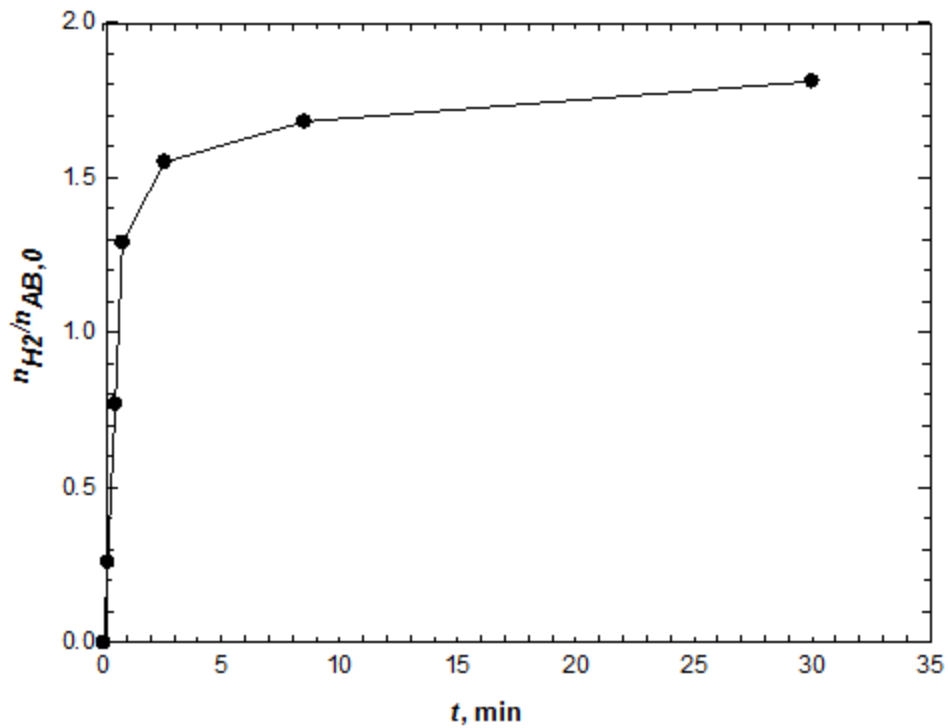
Neat AB thermolysis system slides start here (one slide from UW)

Design objective:

A batch system for neat AB thermolysis at 428 K (155°C) using one gram of AB per batch

Design considerations:

- Use bench top-scale experimental data
- Ease of handling to/from glove box
- Ease of installation in the test cell
- Highly reproducible & controlled batch reactions
- Safety

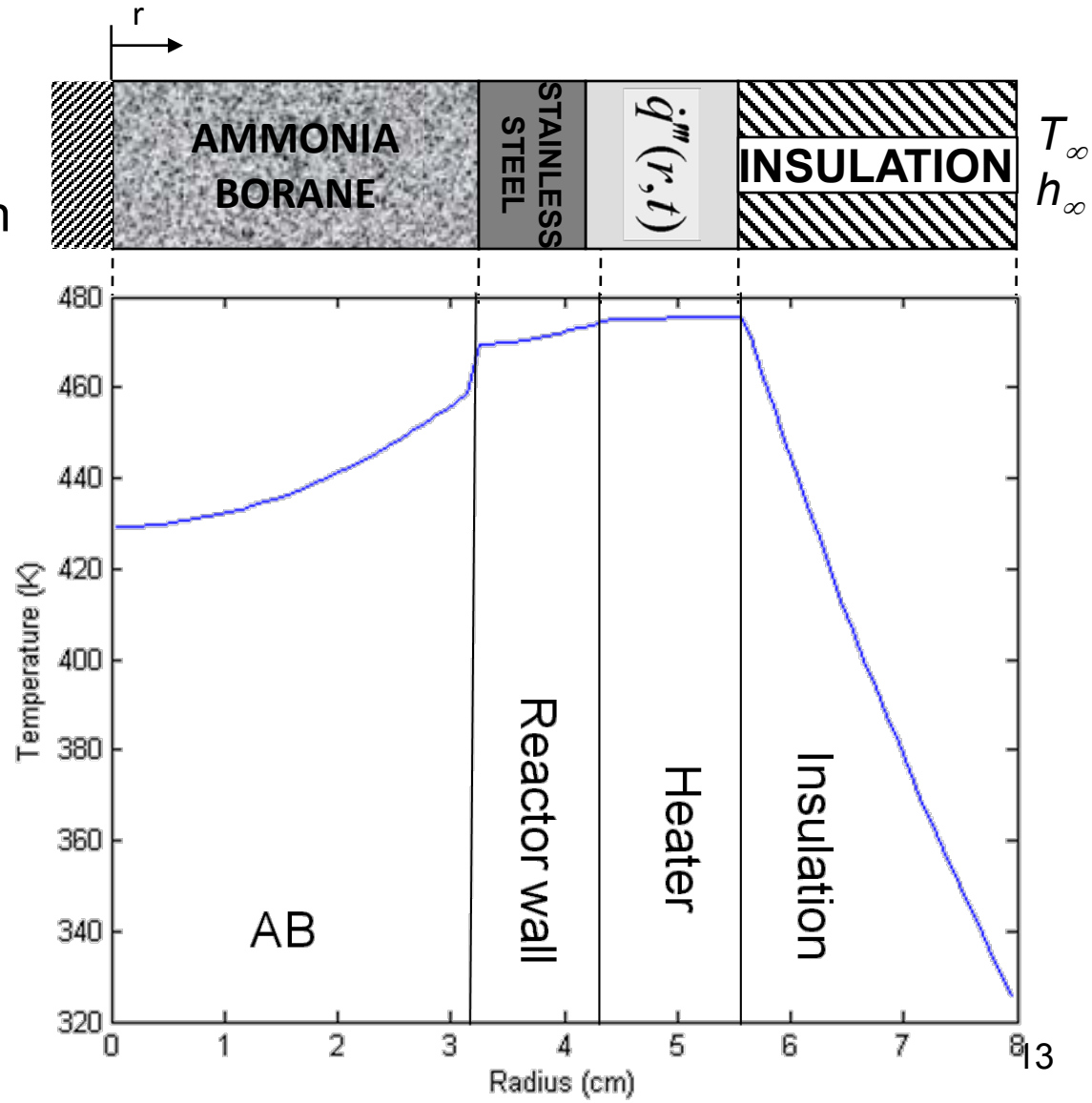


Kinetics of neat AB thermolysis observed with a batch size of 0.13 g AB and a starting temperature of 428 K (155°C) (Experimental data obtained at Purdue University – Fall 2009).

Technical Accomplishments and Progress (cont'd)

- Developed transient 1-D energy model with constant material properties for reaction chamber and heater sizing

- Main Results:
  - Determined temperature profile in 1-D reactor after 13 minutes with 160 W heater (right-hand side)
  - Characterized effect of initial ambient conditions, heater power, and contact resistance between AB powder and reactor wall ⇒ lessons learned for LabView™ based control system development



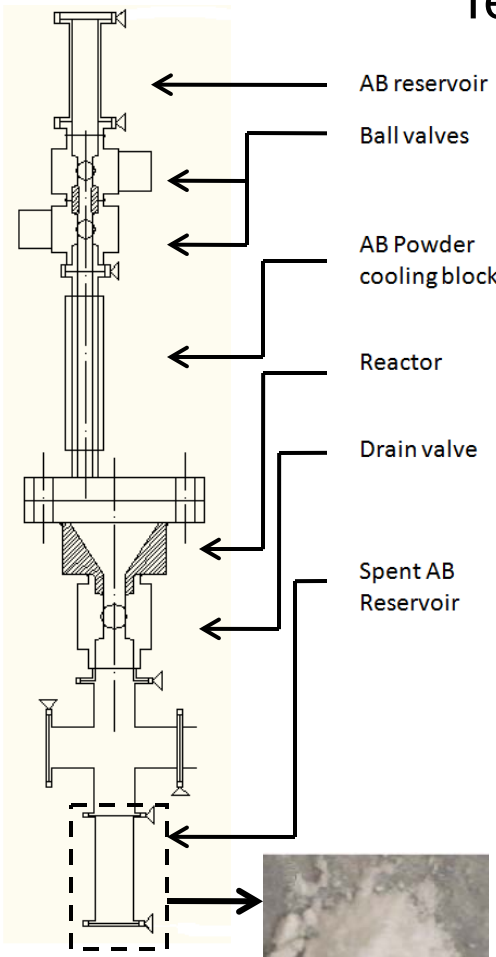
Technical Accomplishments and Progress (cont'd)

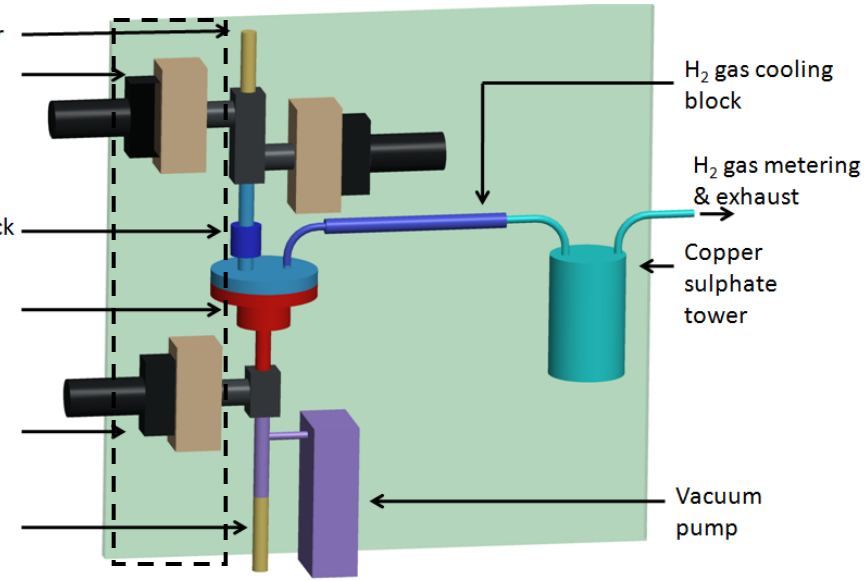
All stainless steel reactor assembly is designed for remote control and monitoring using the Hydrogen Systems Lab data acquisition system.

The AB reservoir and associated ball valves (2) are removable for AB handling in argon glove-box.

Argon filled glove-box
(<0.1 ppm O_2, <0.1 ppm H_2O)

Test Cell Implementation





Planned neat AB reactor components installation in Hydrogen System Laboratory with remote control operation. All components shown to scale.

Spent product from neat AB reactor thermolysis at 120°C; summer 2009 experimental results (Basu et al.)

Technical Accomplishments and Progress (cont'd)

Preliminary AB/BmimCl slurry reactor simulation

Governing Equations

$$\frac{d\dot{m}}{dx} = 0$$

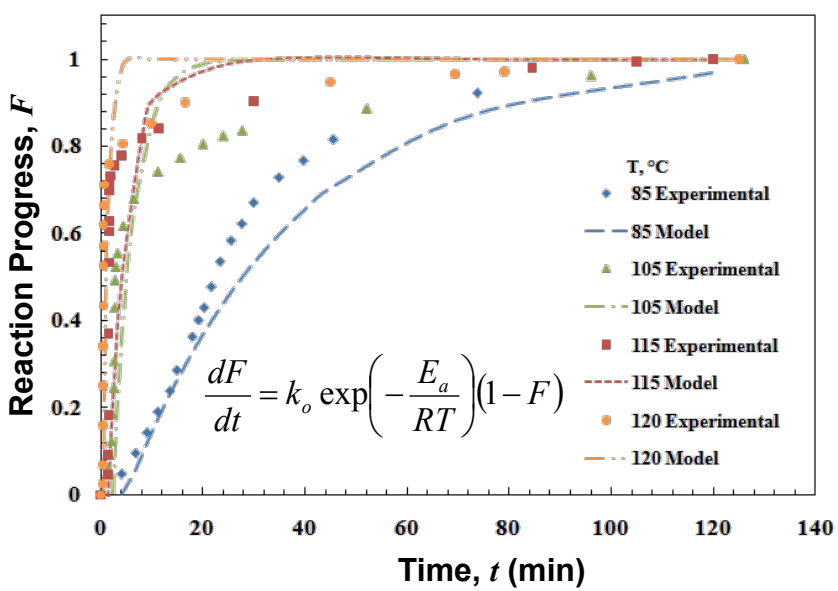
$$\frac{d\dot{m}_s}{dx} = -2MW_{H_2}\dot{R}A_c \qquad \frac{d\dot{m}_g}{dx} = 2MW_{H_2}\dot{R}A_c$$

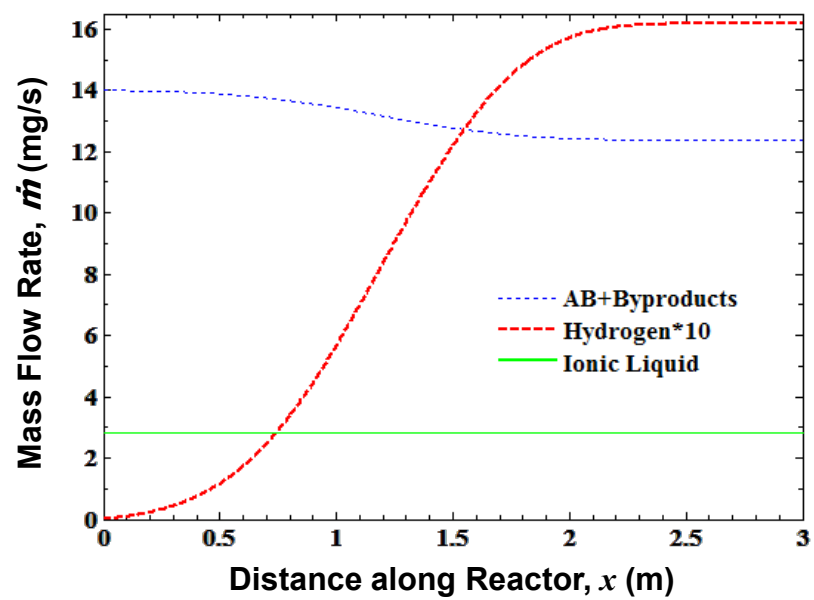
$$\dot{m}\frac{du}{A_c dx} = -\frac{dp}{dx} - \frac{\rho u^2 f}{2D}$$

$$\left(\dot{m}_l C_{p,l} + \dot{m}_s C_{p,s} + \dot{m}_g C_{p,g}\right)\frac{dT}{A_c dx} + 2MW_{H_2}\dot{R}T\left(C_{p,g} - C_{p,s}\right) = q_s''\left(\frac{P}{A_c}\right) + \dot{R}\Delta H_f^o$$

AB slurry reactor (shell-tube type)

Full H_2 flow rate, $\dot{m}_g$ (g/s)	1.6
Full fresh slurry flow rate, $\dot{m}_s$ (g/s)	16.0
AB conversion at the exit, %	95
Tube length, *L* (m)	1.5 x 2
Tube inner diameter, *d* (m)	.025
Shell diameter, *D* (m)	.125





Technical Accomplishments and Progress (cont'd)

Noncatalytic AB hydrothermolysis - experimental

Thermolysis

$$NH_3BH_3 \rightarrow \frac{1}{x}(NH_2BH_2)_x + H_2; \qquad (90\text{-}117\,^{o}C)$$

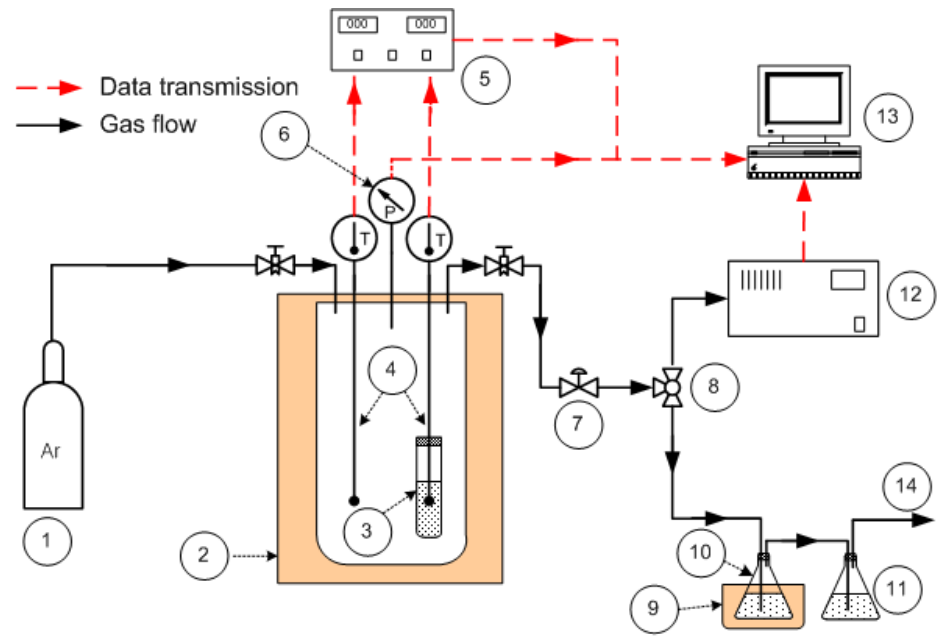
$$\frac{1}{x}(NH_2BH_2)_x \rightarrow \frac{1}{x}(NHBH)_x + H_2; \qquad (150\text{-}170\,^{o}C)$$

Hydrolysis

$$NH_3BH_3 + 4D_2O \xrightarrow{\text{catalyst}} NH_3DB(OD)_4 + 3HD$$

- **Isotopic** experiments were conducted to understand **reaction mechanism** in aqueous AB solutions.
- AB hydrothermolysis experiments were conducted at different temperature (85-135 ^{o}C) and pressures (1-15 atm).
- It was shown that heating aqueous AB solutions and slurries over wide ranges of process parameters results in **significant hydrogen release** from AB and water.

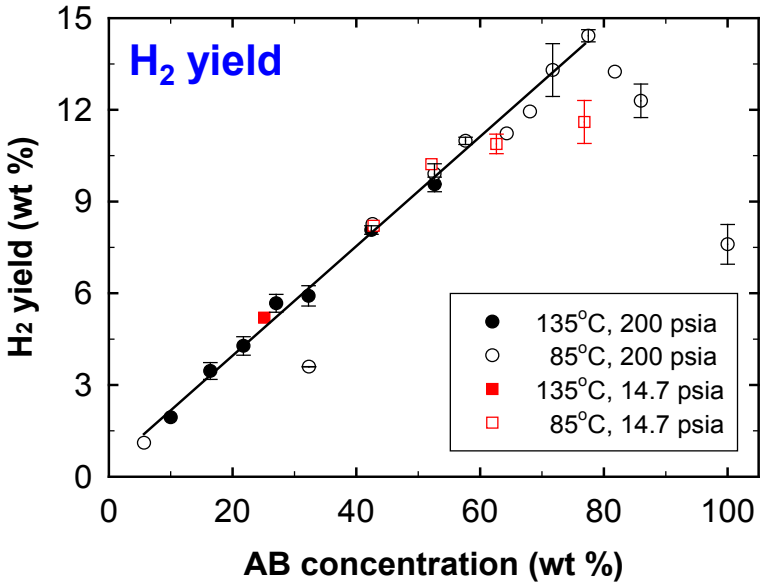
Schematic of reactor setup

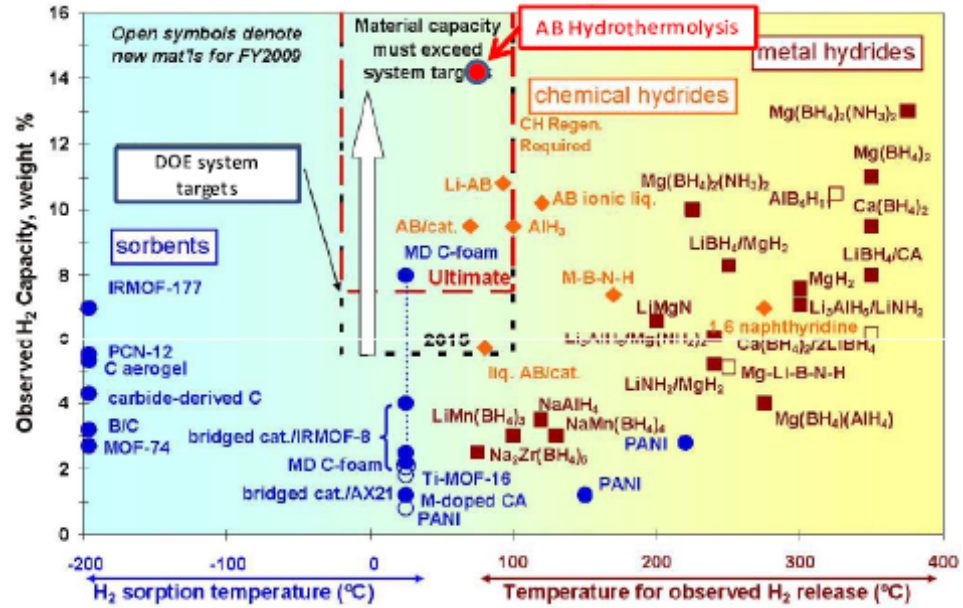


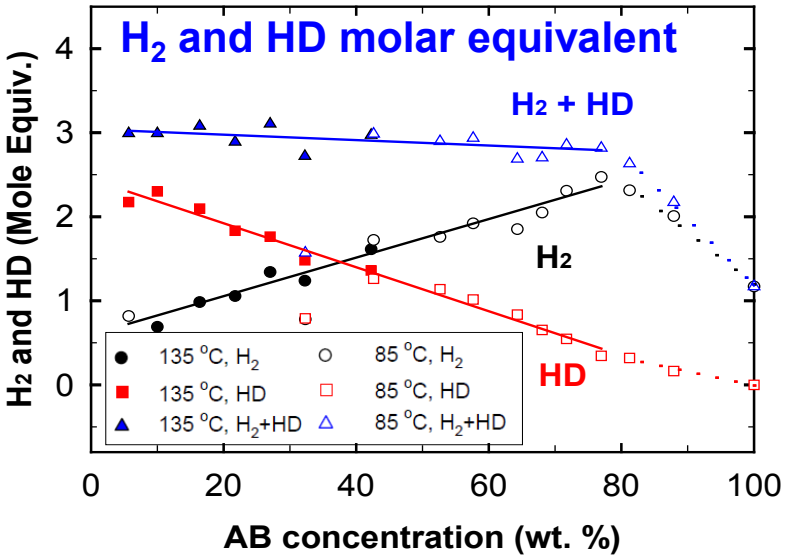
1. Gas cylinder
2. Heating jacket
3. Sample container
4. Thermocouple
5. Temperature controller
6. Pressure transducer
7. Gas flow regulator
8. 3-way valve
9. Dry ice bath
10. Flask with methanol
11. Flask with $CuSO_4$
12. Mass spectrometer
13. Data acquisition system
14. Gas ventilation

Diwan, Diakov, Shafirovich and Varma, *Int. J. Hydrogen Energy,* 33:1135, 2008.
Diwan, Hwang, Al-Kukhun and Varma, *AIChE J., 2010 (in press).*

Technical Accomplishments and Progress (cont'd)

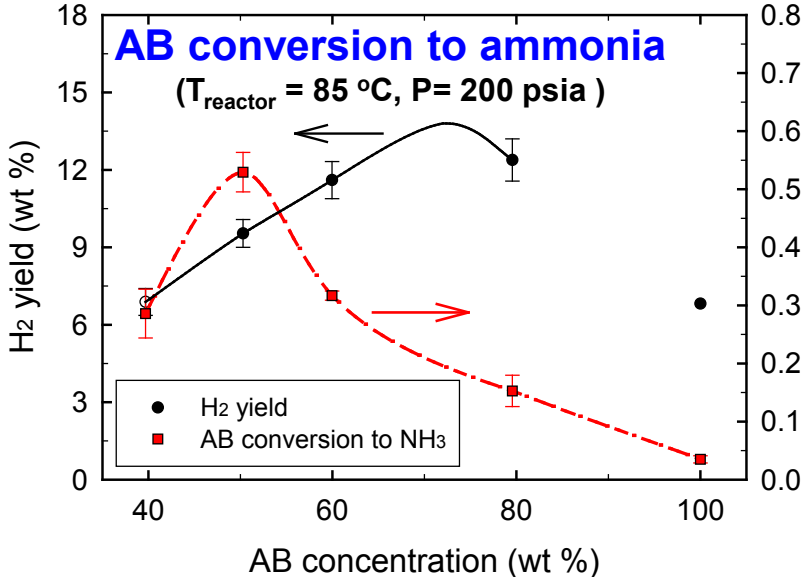


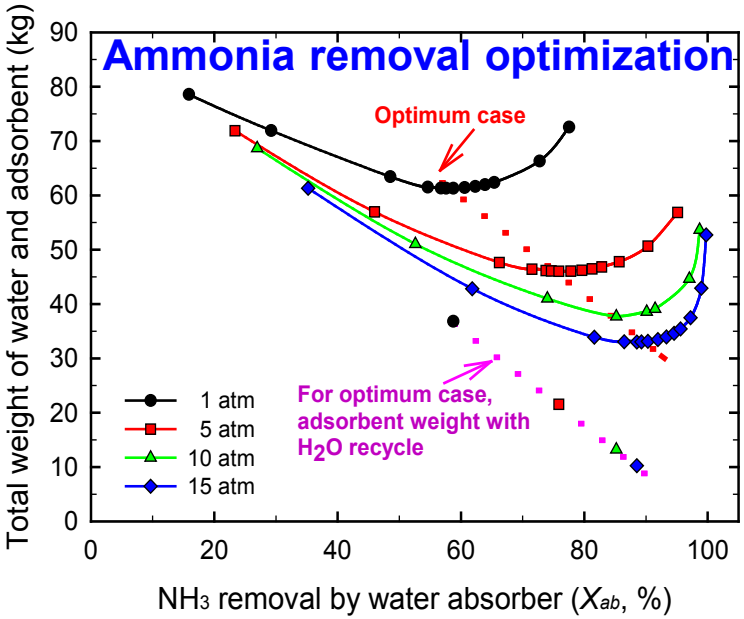




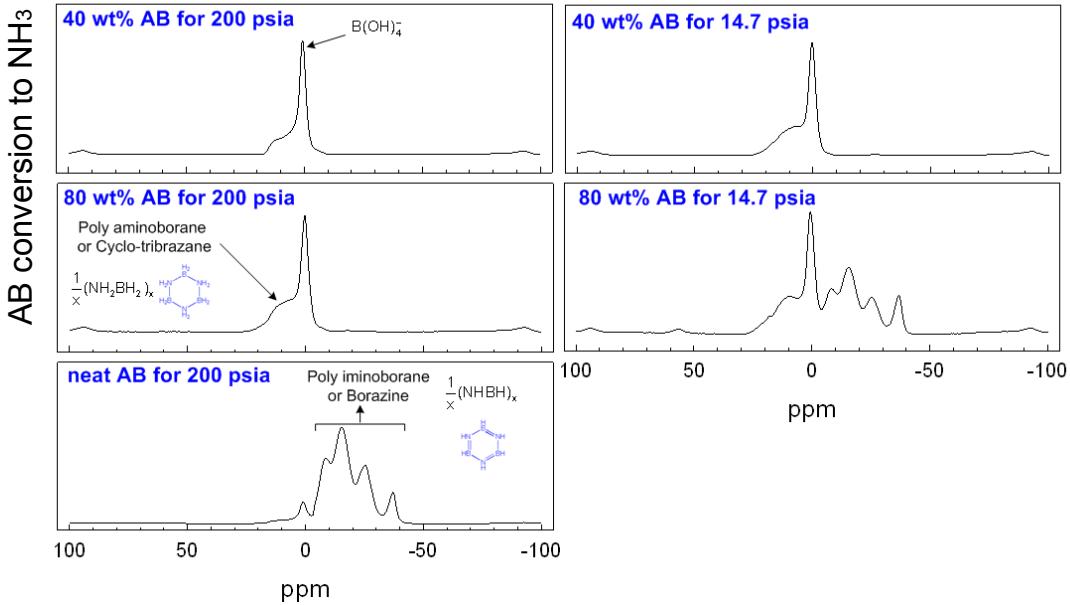
- Hydrogen yield varies linearly with AB concentration for < 77 wt% AB.
- Maximum hydrogen yield determined to be **14.3 wt%.**
- Although H_2 and HD yields vary with AB concentration, the total hydrogen yield (H_2+HD) remains at 2.8 - 3 molar equivalent (for < 77 wt% AB).
- Temperature of 85 °C is sufficient to obtain hydrogen yield > 8 wt % for AB concentration > 43 wt%.
- **AB hydrothermolysis** method has a material capacity that **exceeds the 2015 target significantly**.

Technical Accomplishments and Progress (cont'd)





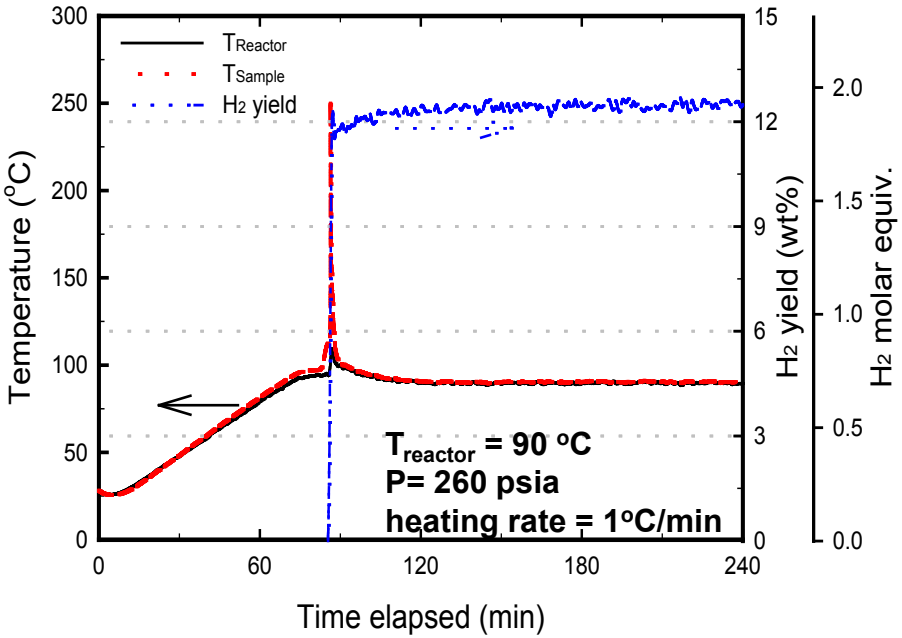
Product characterization using ^{11}B NMR



- Ammonia conversion varies between 53% – 2% from 50-100 wt % AB.
- Some ammonia is observed even for neat AB thermolysis.
- Ammonia can be removed by absorption in water followed by adsorption (activated carbon).
- Ammonia removal increases with pressure.
- For each pressure, an optimum ratio of NH_3 removal by water and adsorbent exists, which minimizes system weight.
- NH_3 removal system weight deceases significantly with water recycle.

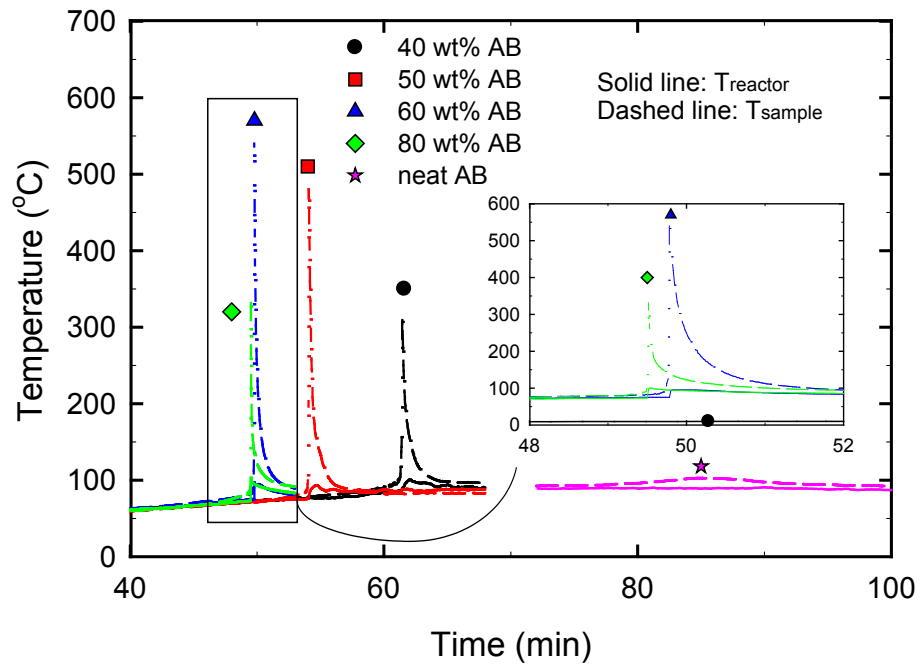
Technical Accomplishments and Progress (cont'd)

Neat AB thermolysis



- Hydrogen yield **>12 wt%** at T ~ 90 °C was obtained with rapid kinetics from neat AB thermolysis at P_i = 260 psia.

Thermal Characteristics: Hydrothermolysis



- $T_{sample,\ max}$ increases with increasing AB concentration up to 60 wt %, and decreases with further increase in AB concentration.
- Sample temperature can reach ~ 500°C.

Collaborations

Purdue University

- Rheology measurements of AB slurry and its hydrolysis byproduct
  with Prof. O.H. Campanella,
  Department of Agricultural and Biological Engineering, Purdue University.
- Kinetics modeling of AB hydrolysis
  with Prof. W.N. Delgass
  School of Chemical Engineering, Purdue University.

Outside Purdue University

- Hydrogen Systems Laboratory facility development
  Chemical and Environmental Science Laboratory
  General Motors Research & Development Center.
- Ammonia borane synthesis
  General Atomics.

Future Work

AB Recycling

- The calculation of the bond energies for the proposed AB recycling is under way.
- The reduction of tris-acylborates using silanes will be optimized to avoid over reaction and charring.
- The conversion of ammonium borate or $B(OH)_3$ to $B(OR)_3$ will be carried out.

Dehydrogenation of AB Slurry

- Investigate the non-Newtonian behavior of the fresh and spent fuel flows and simulate the thermo-fluid processes in the fuel tank, the gas/liquid separator, and the recuperator.
- Measure hydrogen yield and characterize operation of 1-gram scale neat AB reactor
- Apply lessons learned with the neat AB reactor to the design of the AB slurry reactor

Investigation of Noncatalytic AB Hydrothermolysis

- Determine the optimal conditions where the hydrothermolysis process provides the best balance between H_2 yield and undesirable products.
- Investigate AB hydrothermolysis in liquid carriers at different operating conditions, and evaluate neat AB thermolysis.
- Develop and test performance of prototype hydrogen generation and fuel cell system.

Project Summary

AB Recycling

- AB was prepared in kilogram scale from sodium borohydride and ammonium sulfate in the presence of ammoniated THF at room temperature in 92% yield and ≥ 98% purity.
- Trimethylborate was reduced using diethylsilane in the presence of TMEDA to TMEDA-Bisborane complex.
- TMEDA-Bisborane complex was converted to AB via transamination in 80% yield.

Dehydrogenation of AB Slurry

- Completed a preliminary simulation of a full scale AB slurry reactor using measured AB/BmimCl slurry thermolysis kinetics data.
- Designed a 1-gram scale neat AB reactor at the Hydrogen Systems Laboratory and developed critical design review package for internal review.

Investigation of Noncatalytic AB Hydrothermolysis

- The maximum hydrogen storage capacity obtained at 77 wt% AB concentration and $T_{reactor}$ ~85°C, was 11.6 and 14.3 wt% at pressure 14.7 and 200 psia, respectively.
- Ammonia generation was observed for AB hydrothermolysis as well as neat AB thermolysis.
- Rapid hydrogen release kinetics were observed for AB hydrothermolysis.